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CONTROL OF ELECTRONIC MAGNETIC AND OPTICAL PROPERTIES
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DEPT OF PHYSICS A J HEEGER 01 OCT 82 ARO-17716.7-MS
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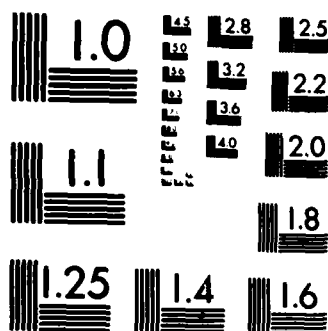


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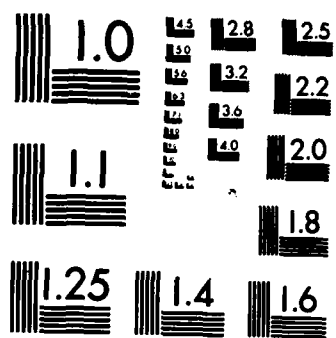
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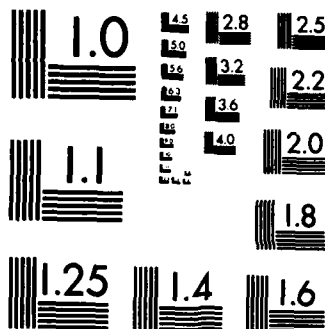
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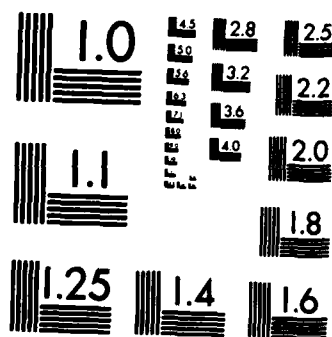
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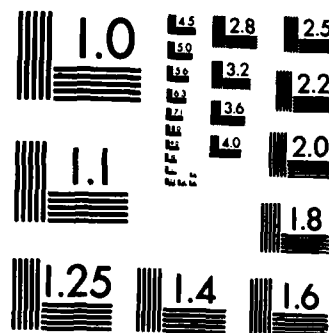
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Control of Electronic, Magnetic and Optical Properties
of Doped Polyacetylene Conductors through Induced Defects

FINAL REPORT

October 1, 1982

U. S. Army Research Office

Contract Number: DAAG29-81-K-0058

Department of Physics
University of Pennsylvania
Philadelphia, PA. 19104

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The experimental studies carried out under this program focused on the use of particle irradiation to induce defects in polyacetylene. The program evolved into a related detailed study of the photoexcitations in (CH_x) including luminescence, photoconductivity and Raman scattering. (C) DB X		

A. Statement of the problem studied

Polyacetylene has been the center of considerable attention, because of the novel fundamental physics which governs its properties and because of its potential usefulness in technology as an electronic and electrochemical material. As an electrochemical active material, $(CH)_x$ electrodes have been used to fabricate high energy density, high power density electrochemical cells. As an electronic material, the energy gap and large bandwidth of polyacetylene are comparable to those of other potentially useful large scale thin film semiconductors such as amorphous silicon. Moreover, a variety of simple junction devices made with $(CH)_x$ have been reported. Post-synthesis doping at room temperature has been demonstrated using both chemical and electrochemical techniques. This ability to dope polyacetylene with relative ease after synthesis primarily arises from the morphology of the polymer, which consists of microcrystalline fibrils with a high surface area.

Although considerable progress has been made in understanding the basic physical properties of this interesting material, the absence of experimental results from single crystal samples has generated controversy in the interpretation of the results. As an alternative approach to improving the crystallinity and sample perfection of polyacetylene we have monitored its physical properties as a function of irradiation by high energy C^{+6} heavy ions.

Through the initial idea of monitoring the chain length by Raman scattering after particle irradiation, the program

evolved into detailed studies of the nature of the photo-excitations in polyacetylene; including luminescence, photoconductivity and Raman scattering.

B. Summary of most important results

I. Irradiation Studies of Polyacetylene

A study of $(\text{CH})_x$ and $(\text{CD})_x$ irradiated with high energy C^{6+} ions showed the polymer to be remarkably resistant to radiation damage. Despite the large doses, up to $10^{14} \text{C}^{6+}/\text{cm}^2$, no significant structural effects were observed. On the other hand, a large increase (3-4 orders of magnitude) were seen in the resistivity upon irradiation for trans, with $(\text{CH})_x$ showing roughly one order of magnitude higher increase over $(\text{CD})_x$. The lack of concurrent structural effects and the high conductivities observed in the films doped after irradiation imply the increase in resistivity is due to the compensation of impurities as a function of increasing dose. A very unusual isotope effect was seen, where the resistivity of $(\text{CD})_x$ decreased (by ~ 1 order of magnitude) for doses above $\sim 10^{13} \text{C}^{6+}/\text{cm}^2$. This decrease is quite remarkable, not only unlike $(\text{CH})_x$, but unlike any other organic conductor. Although this behavior is not yet understood in a microscopic model, it may be due to the different diffusing rates of hydrogen and deuterium in polyacetylene.

II. Photoexcitation in Polyacetylene

The results of experimental studies of photoluminescence and photoconductivity in cis- and trans- $(\text{CH})_x$ were presented. For cis- $(\text{CH})_x$, we found recombination luminescence in the scattered light spectrum at 1.9 eV, near the interband

absorption edge. The luminescence turns on sharply for excitation energies greater than 2.05 eV, implying a Stokes shift of 0.15 eV. Studies of the temperature dependence ($T \geq 7K$) show no loss of luminescence intensity even at temperatures as high as 300K. Isomerization of the same sample quenches the luminescence; we find no indication of luminescence near the interband absorption edge of trans-(CH)_x even at temperature as low as 7K. These results are discussed in the context of parallel phototransport studies. The quenching of the luminescence upon cis-trans isomerization is concurrent with the appearance of a large photoconducting response. The photoconductivity in trans-(CH)_x has a threshold at 1.0 eV, well below the interband absorption edge at 1.5 eV, implying the presence of states deep inside the gap. The observation of luminescence in cis-(CH)_x, but not in trans-(CH)_x; and the observation of photoconductivity in trans-(CH)_x, but not in cis-(CH)_x provide confirmation of the proposal that solitons are the photogenerated carriers. In trans-(CH)_x, the degenerate ground state leads to free soliton excitations, absence of band edge luminescence, and photoconductivity. In cis-(CH)_x the non-degenerated ground state leads to confinement of the photogenerated carriers, absence of photoconductivity and to the observed photoluminescence.

III. Absolute Raman Scattering Cross-Sections of trans-(CH)_x

Measurements of the absolute Raman cross-sections for trans-(CH)_x are reported. The results have been analyzed to study the contribution of hot luminescence to the inelasticity

scattered light spectrum. The magnitude and frequency dependence of the absolute scattering cross sections are consistent with hot luminescence being the dominant process. To determine the contribution of static resonance effects (i.e. short chains) to the Raman lineshape, we presented sliced excitation profiles. We found no evidence for the resonance behavior of short chains.

IV. Laser Micro-Raman Scattering of Polyacetylene.

The first laser micro-Raman spectra of polyacetylene have been observed. Using an ISA Raman microprobe, the sample is positioned on the stage of a research grade optical microscope and the exciting radiation is focused to a 1 to 10 micron spot on the sample. The Raman backscattered radiation is then collected by the microscope and imaged into the entrance slits of a standard double monochromator with photon counting detection. Micro-Raman spectra from free standing polyacetylene films revealed similar lineshape profiles as the laser beam was scanned across the surface of the film. However, changes in the lineshape profile between the front and back surfaces of the films have been observed. The specialized features of the micro-Raman technique (allowing examination of very small areas) has been used to characterize and unambiguously identify epitaxial films of oriented $(CH)_x$.

C. Publications

- 1) The Effect of C^{+6} Irradiation on Transport Properties of $(CH)_x$ and $(CD)_x$
Bull. Am. Phys. Soc. 26, 346 (March, 1981)
- 2) Photoexcitations in Polyacetylene
Phys. Rev. B24, 1, 1981

- 3) Electronic Excitations in Polyacetylene
Molecular Crystals and Liq. Crystals 77, 54 (1981)
- 4) Absolute Raman Scattering Cross-Sections of
trans-(CH)_x, Phys. Rev. B (in press)
- 5) Polyacetylene, (CH)_x: The Prototype Conducting
Polymer Annual Review of Physical Chemistry
Vol. 33 (in press).
- 6) Evidence for Polarons in trans-polyacetylene,
trans-(CH)_x: An Optical Study Phys. Rev. B
(in press)

D. Participating Scientific Personnel

A. J. Heeger, Professor of Physics

S. Etemal, Visiting Assoc. Professor of Physics

L. Lauchlan, graduate student

Dr. Lauchlan earned her Ph.D. on the research supported by this grant. Her thesis was completed in July, 1982 with the title:
"Photoexcitations in Polyacetylene".